Western Michigan University
ScholarWorks at WMU

Paper Engineering Senior Theses

Chemical and Paper Engineering

1960

The Bleaching of Groundwood

Dale C. Hedquist
Western Michigan University

Follow this and additional works at: https://scholarworks.wmich.edu/engineer-senior-theses

Part of the Wood Science and Pulp, Paper Technology Commons

Recommended Citation

Hedquist, Dale C., "The Bleaching of Groundwood" (1960). *Paper Engineering Senior Theses*. 290.
https://scholarworks.wmich.edu/engineer-senior-theses/290

This Dissertation/Thesis is brought to you for free and open access by the Chemical and Paper Engineering at ScholarWorks at WMU. It has been accepted for inclusion in Paper Engineering Senior Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact maira.bundza@wmich.edu.

The Bleaching of Groundwood

by

Dale C. Hedquist

Independent Study 499

Western Michigan University
Kalamazoo, Michigan

ABSTRACT

Present industrial methods for the bleaching of groundwood are discussed. The conditions and chemicals used for hypochlorite, sodium and zinc hydrosulphite, bisulphite and sodium and hydrogen peroxide bleaching are reviewed. Consistencies, retention time, pH and temperature for maximum brightness are discussed for each process. Chemical reactions for the removal of color are given for several of the processes.

TABLE OF CONTENTS

HISTORY

Color of wood is dependant upon non carbohydrate content such as extraneous compounds (1). Lignin is considered to be white in its native state but contains reactive sites that can be easily converted to chromophonic groups. Mechanical pulping provides high temperatures and increased surface area, which is ideal for air oxidation and color development. Since the principal advantage of mechanical pulps are their high yields it is necessary to remove the color without dissolving the lignin itself.

Groundwood pulps when made from certain wood species provide an adequate background for printing newsprint without bleaching. Certain papers made from groundwood pulps require higher brightness base stock. The first attempts to increase brightness of groundwood pulps utilized raw cooking acid[1] as a bleaching agent. The acid was added to the pulp on a wet lap machine. Brightness increases were small and by no means permanent.

The reducing agents zinc and sodium hydrosulphite were the next development in the bleaching of groundwood. The hydrosulphites gave a greater increase in brightness and permanence. Hydrosulphites are purchased in the zinc or sodium salt. Zinc hydrosulphite can be formed by passing sulphur dioxide into a water slurry of zinc dust.[1,3]

$$Zn + 2H_2SO_4 = ZnS_2O_4 + 2H_2O$$

The sodium and hydrogen peroxides are especially adapted to the bleaching of groundwood pulps. Peroxides impart a significant increase in brightness and can be used alone or in combination with hypochlorites. Peroxides have been used in the bleaching process since the early 20th century but haven't found use in our industry until the 1940's. By 1950 the process was in use in 24 mills within the U.S.[1]

REDUCING AGENTS

Sodium bisulphite, and sodium and zinc hydrosulphite, and sulphurous acid have all been used for bleaching groundwood. This is not pulp purification in the sense of regular bleaching since there is no removal of material from the pulp. The bleaching effect of bisulphite is of a low degree compared to other methods. One to two percent bisulphite results in a 2-4 point increase in brightness. Temperature and consistency have little effect on final brightness. It is usually applied on a wet lap machine but can be added to the thickened pulp chest.[1,3]

Zinc and sodium hydrosulphites are used to a greater extent. They are equivalent in brightness improvement but zinc hydrosulphite imparts a better permanance. The cost of bleaching with hydrosulphite is lowest of the methods usedfor groundwood but a brightness increase of 8-10 points is maximum.[3,14] The important variables are consistency, pH, temperature, time, concentration, and iron content of the wood species.[11] Consistencies of 1 to 6% are generally used but the maximum limit is about 15%. For each 20-25° F There is approximately one point increase in brightness. Temperatures between 100-180° F are generally used. Deterioration of color may take place if the pulp is held too long at very high temperatures. Most of the brightness gain is attained in the early stages of bleaching. Optimum pH is between 6-7. At pH's below 4.5 the hydrosulphite decomposes and above 6.5 yellowing occurs. Iron contaminates are very detrimental. Iron reacts with the lignin degradation products and form dark colored compounds.[1,3] Sequestering agents such as ethylenediaminetetraacetic acid are used to prevent this.[12] Hydrosulphites hydrolyze as follows;

$$1.\quad S_2O_4^{-2} + 2H_2O \longrightarrow 2HSO_3^{-1} + 2H^+$$

2. $S_2O_4^{-2} + 2H_2O \longrightarrow S_2O_6^{-2} + 2H^+$

3. $S_2O_4^{-2} + 3H_2O \longrightarrow HSO_3^{-1} + HSO_4^{-1} + 4H^+$

4. $S_2O_4^{-2} + 4H_2O \longrightarrow 2HSO_3^{-1} + 6H^+$

5. $2S_2O_4 + H_2O \longrightarrow S_2O_3^{-2} + 2HSO_3^{-1}$

6. $S_2O_4^{-2} + H_2O + O_2 \longrightarrow HSO_3^{-1} + HSO_4^{-1}$

H+ ions released react with pulp to reduce color components. If free oxygen is present the H^+ will oxidize before reaction can occur. Therefore entrapped O_2 must be kept to a minimum. Hydrosulphite is usually added at the suction pump before entering the bleach tower.[14]

PEROXIDE BLEACHING

The modern concept of the mechanism of peroxide bleaching is:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

The HO_2^- is considered the active bleaching agent. The reaction is reversible but is forced to the right with alkalis. The alkali removes the ^+H ions and forces the reaction to the right. Peroxide may decompose under certain conditions into water and free O_2:[1, 3]

$$2H_2O_2 \rightleftharpoons 2H_2O + O_2$$

This reaction is promoted by heavy ions such as iron, copper, and manganese.[2,3] Magnesium sulphate and sodium silicate are added to the peroxide to inhibit catalytic effects.[3,6]

The peroxide bleaching process consists of four steps:[3]

1) Preparing the bleach liquor
2) Rapid and thorough mixing of the bleaching sodium
3) Storage until bleaching has gone to completion
4) Neutralizing residual peroxide with a reducing agent.

Typical bleach liquor formulas can be found in table I.[5]

Table I

Bleach Liquor Formulas

	1% Bleach	2% Bleach	3%Bleach
Total no. of gallons of bleach paper	3000(4500)	4500	4500
Sodium Peroxide, lb.	400(800)	800	800
Hydrogen peroxide, lb.	217(0)	180	466
Silicate of soda, lb.	3940(4000)	2540	2260
Epsom Salts, lb.	20(40)	26	22
Equivalent sodium peroxide/100 gal.	21.8(17.8)	22.5	30.1
Gallons bleach liquor/ton of pulp	92(112)	177	199

Results depend on species of wood, age, and conditions of bleaching.[1,8] Generally the amount of peroxide used is between 1 and 2%. For example, using sodium hydroxide at 90 degrees F. and 5% consistency[9]

% Sodium Hydroxide	Increase in Brightness, GE
1.0	6-7
1.5	8-9
2.0	10-11

PH is generally kept at 10.5 or higher. Since ground wood is acidic(pH 4.5-5.0)alkali has to be added. Buffered or bound alkali systems are generally used because they release alkali slowly through the bleaching period.[3]

Sodium silicate is used extensively for this purpose. It acts as a wetting agent or metal surface passivator and stabilizer.[7,8]

Temperature is maintained in a range of 40-60 degrees C.[10] Higher consistencies up to 35% generally require less bleaching time than the lower consistencies3-6%.[3] There is a straight line relationship between brightness increase and pulp consistency when a constant amount of stock is used.[10] A graph of Hunter brightness is shown on Fig. I.

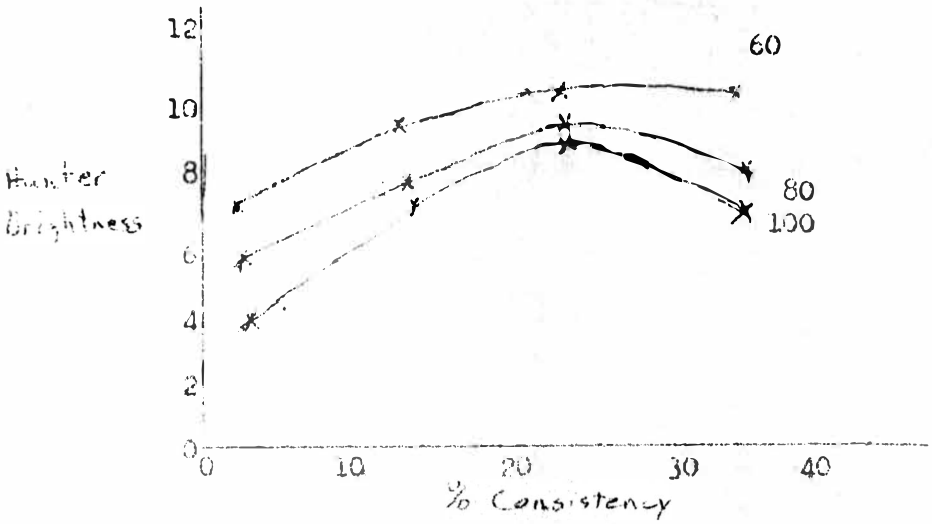

Fig I.

Effect of Consistency and Temp. on brightness of Peroxide bleached ground wood

Industrially higher consistencies offer improved chemical efficiency with decresed bleaching costs, and shorter retention times to achieve equivalent brightness levels.

At the end of the bleaching period, a neutralizing agent is is added to remove residual peroxide. By bringing the pH up to 5.5-6.5, brightness will increase. Sulphurous acid is generally used for this purpose.[3]

Peroxides can be purchased as either hydrogen peroxide or sodium peroxide. One pound of sodium peroxide is equivalent in active oxygen content to 1.21 lb. of 35% hydrogen peroxide plus 1.02 lb. of sodium hydroxide.

Peroxide bleached grounwood has all the good qualities of regular groundwood, including high opacity, high bulk, resiliency and good covering properties and in addition has a much better brightness. Stability is not greatly improved when stored in in light but is very good when stored away from light.[10] Bleached groundwood has a slower drainage rate than unbleached and improved formation is usually noted on the paper machine.[3] Paper made from bleach groundwood is finer, more homgeneous and smoother than regular groundwood papers. These factors make for better print quality.[3] Groundwood yield loss is from 3-4% with peroxide. Peroxide decolors lignin like hypochlorite.[7]

HYPOCHLORITE

Hypochlorite is another groundwood bleaching chemical. It is used on hardwood mechanical pulps and is quite effective. Brightness of 70-75 can be achieved with charges of 10% available chlorine.[3] Retarding the rate of reaction in the initial stages is essential. This is accomplished by maintaining temperatures at about 25-35 degrees C. The density should not exceed 6% and pH should be 11-12 at the start of the reaction and no less than 8 at the end.[4] Sodium silicate is used as a buffer for the alkali. Finally, the reaction should be stopped short of complete chlorine utilization.[3]

Yields of hardwood groundwood are in the range of 96-100%. The brightness gained is not stable but the strength is relatively good.[3] Hypochlorite is a strong oxidizing chemical and reacts with pulp impurities to form white or water soluble products.[14]

Lignin (dark colored) + Hypochlorite → Lignin Oxide (white or soluble) + calcium chloride.

Bibliography

1) Bleaching of Pulp. TAPPI Monograph.

2) Reichert, J.S., Campbell D.J., and Secord R.A., Paper Trade Journal; 119, NO. 16:49-51(Oct. 1944)

3) Casey, J.P., Pulp and Paper Chemistry and Technology, second edtion; Volume 1.

4) Kingsbury, R.M., Lewis E.S., and Simmonds. Paper Trade Journal; 126, No.24:272-276. (June 10, 1948)

5) Boyer, H.J. TAPPI 39; No. 5, 180 A-182 A. (May 1956)

6) Reichert, J.S., Campbell D.J., and Mills, R.T., Paper Trade Journal; 118, No. 15: 125-128. (April 13, 1944)

7) Stove, M.L., TAPPI 48, No. 9:534-535. (Sept. 1965)

8) McEwen, R.L., Paper Trade Journal; (Nov. 14, 1952)

9) Reichert J.S., Paper Trade Journal; 105. No. 15:143-148. (April 12, 1945)

10) McEwen, R.L., Paper Trade Journal; 122. No. 17:179-183. (April 25, 1946)

11) Rittenhouse, G.W., TAPPI, 37; No. 5: 170A-171A. (May 1954)

12) Sparrow, D.B., Ebert J.J., and Britt K.W., U.S. Pats. 2,707,144 and 2,707,145.

13) Barton, R.W. TAPPI 44, No. 8:161A. (Aug. 1961)

14) Bodenheimer, V.B., Enloe, J.O., Southern Pulp and Paper Manufacturer. (April 1976) p. 30-39.